

PATENT SPECIFICATION

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(54) POLYMER COMPOSITIONS FOR ELECTRICAL USE

(71) We, RAYCHEM LIMITED, a British Company, of Moor House, London Wall, London, E.C.2, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymer compositions for electrical use and is related to our copending application Nos. 13352/73, 49724/76 and 49725/76 (Serial Nos. 1 470 501, 1 470 503 and 1 470 504).

In a continuously shielded or screened high voltage cable, the electric field is uniform along the cable axis, and there is variation in the field only in the radial direction. The spacing of the electric flux lines and the equipotential lines are closer in the region of the conductor than elsewhere, as shown by the following equation:

$$E_x = \frac{V_o}{x \ln (R/r)}$$

where

E_x =electrical stress at point x , in volts/mil

x =distance from centre of cable in mils

V_o =applied voltage in volts

R =radius of cable over insulation

r =radius of cable conductor

Thus the stress is a function of the geometry of the cable and in practice the insulation thickness is sufficient to maintain the stresses at acceptable levels for the dielectric concerned.

When such a cable is terminated, the screen or shield is removed for such a distance that electrical breakdown along the surface of the insulation from the conductor to the shield or screen cannot occur. The removal of this screen or shield causes discontinuity of the electrical field so that there is severe electrical stress at the point of the end of this screen or shield. In order to relieve this stress and so prevent failure of the cable and termination in service, a number of methods have been developed to provide adequate stress control. Among these methods may be mentioned the use of stress cones, (pre-moulded or fabricated type), resistive coatings and non linear tapes.

Stress cones extend the shield or screen of the cable by the use of a conducting material such as wire, metal foil or tapes on part of the surface of an insulating cone. The cone may be made from tapes of plastic or paper, epoxy resins, rubbers etc. Stress cones thus expand the diameter of the cable at the discontinuity and hence reduce the stress. They thus require considerable space over and above the cable diameter and usually require skill and time during fabrication on the cable.

Pre-moulded stress cones of the slip-on type may also be used, but their interference fit characteristics mean that both cable and cone have to be made to close tolerance for optimum performance. It has also been proposed to make stress cones by the build up of layers of different lengths of heat shrinkable tubing, but such cones are not very practical as this method is very time consuming and introduces the possibility of interlaminar voids.

Resistive coatings on the surface of the insulation from the conductor to the shields will reduce the stress by conducting sufficient current to establish a substantial

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linear distribution of voltage. The high resistance necessary to achieve this and to avoid dissipating an excessive amount of power is rather critical and must remain a constant value in service in order to be satisfactory. This is very difficult to achieve in practice and such coatings are not now in general use.

Coverings of preformed sleeves, wrapped tapes such as these based on PVC, or dry coatings, having a non linear electrical resistance characteristic, have also been proposed to provide stress control. These coverings have the disadvantage that, in general, effective stress control is obtained only by careful and skilful application of the covering and that the materials age rapidly at elevated temperatures, such that cracking occurs in the coating layer thereby destroying the effectiveness of the stress control.

It has been proposed also to use, as a material having non-linear electrical resistance characteristics, a potentially heat shrinkable polymer having dispersed therein particulate silicon carbide. The material may be processed into a heat shrinkable article, for example a tube, by moulding or extrusion coupled with the usual procedures for making polymers heat shrinkable (see for example U.S. Patents Nos. 2,027,962 and 3,086,242). Silicon carbide has the disadvantages that, in the form of the very fine particles preferably used, it is expensive and that, at the relatively high loadings required, for example 40% by volume based on the polymer, processing problems arise on account of the fact that silicon carbide is very abrasive; this may cause considerable wear of process equipment such as internal mixers, two-roll mills and extrusion dies. Furthermore, the non-linear electrical resistance characteristics of the silicon carbide loaded polymers of the prior art cannot be widely varied.

By the term "non-linear electrical resistance," there is meant that the electrical resistance of the material in question varies with voltage across the material i.e. the current I flowing through the material when a voltage V is applied across the material substantially obeys the relationship: $I=KV^\gamma$ where K is a constant and γ is a constant greater than 1. For linear materials, γ is equal to 1.

Thus, there is a need to provide materials which can be used to effect stress control on the surfaces of high voltage insulation without the disadvantages of the articles of the prior art.

According to the invention, there is provided a material comprising a polymer containing at least units derived from propylene and ethylene, the polymer having dispersed therein a particulate filler selected from at least one of the following:

- (a) Compounds having a perovskite type crystal structure.
- (b) Compounds having a spinel crystal structure other than $\gamma\text{-Fe}_2\text{O}_3$ and spinel itself.
- (c) Compounds having an inverse spinel crystal structure.
- (d) Compounds having a mixed spinel crystal structure.
- (e) Dichalcogenides of transition metals and of tin.
- (f) AgI Prussian Blue, Rochelle salt and other alkali metal tartrates, compounds of the formula XH_2YO_4 wherein X is K, Rb or Cs and Y is P or As, for example potassium dihydrogen phosphate, ammonium sulphate, ammonium fluoroberyllate, thiourea and triglycine sulphate ($[\text{CH}_2\text{NH}_2\text{COOH}]_3\text{H}_2\text{SO}_4$).
- (g) Si_3N_4 .

the said particulate filler being present in an amount of at least 10% by weight based on the polymer, and in an amount such that the value of γ at some direct current (DC) electrical stress between 0.01 kV/mm and 10 kV/mm is at least 1.5. Preferably the value γ is at least 1.5 at a direct current (DC) stress between 0.1 and 5 kV/mm.

In addition to the materials listed in (a) to (g) above, the material may comprise one or more particulate electrically conductive fillers.

As compounds of the type (a) above, there may be mentioned, for example, compounds having the general formulae:

- (i) ABO_3 wherein A represents Ca, Sr, Ba, Pb, Mg, Zn, Ni or Cd and B represents Ti, Zr, Hf, Sn, Ce or Tc or A represents a rare earth metal and B represents Al, Se, V, Cr, Mn, Fe, Co or Ga,
- (ii) KBF_3 wherein B represents Mg, Cr, Mn, Fe, Co, Ni, Cu or Zn, or
- (iii) ATiS wherein A represents Sr or Ba, and AZrS wherein A represents Ca, Sr, B.

There may be especially mentioned BaTiO_3 , BaSnO_3 and SrTiO_3 and the following, which are preferably used in admixture with a particulate conductive filler: BaZrO_3 , CaTiO_3 , CaSnO_3 , CaZrO_3 , MgSnO_3 , PbSnO_3 , MgZrO_3 , NiTiO_3 .

and mixed Zinc Titanate (a zinc titanate in which one or more of the zinc or titanium atoms have been replaced by another metal).

As compounds of the type there may be mentioned, for example, compounds having the general formulae:

(iv) $A''B_2'''O_4$, wherein A represents Mg, Mn, Fe, Co, Ni, Cu, Zn or Cd and B represents Al, Cr, Fe, Mn, Co or V, provided that when A represents Mg, B cannot represent Al, or

(v) $A''B'O_4$, wherein A' represents Ti or Sn and B represents Zn or Co, Ni, Mn, Cr, Cd.

There may be especially mentioned $CoAl_2O_4$, $CuCr_2O_4$, $CuMn_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$, Barium and strontium ferrites (e.g. $BaFe_{12}O_{19}$) which are of the magneto plumbite structure (a type of depleted spinel) are also suitable.

As compounds of the type (c) there may be mentioned, for example,

(vi) $Fe'''(Mg''Fe''')O_4$, $Fe'''(Ni''Fe''')O_4$, $Fe'''(Cr''Fe''')O_4$, $Co'''(Co''Sn'')O_4$, $In'''(Mg''In'')O_4$, $Zn'''(Zn''Ti'')O_4$, $Zn'''(Zn''Sn'')O_4$, $Li_2V_2O_4$, $Fe_{2.5}Li_{0.5}O_4$ and, especially, Mn_3O_4 , Co_3O_4 , Fe_3O_4 and slightly non-stoichiometric variants thereof, for example $Fe_2O_3 \cdot 0.8FeO$.

As compounds of the type (d) there may be mentioned, for example, Bayer Fast Black 100 (which results from sintering 50% by weight Cr_2O_3 , 40% by weight Fe_2O_3 and 10% by weight CuO), Bayer 303T (a mixed phase pigment of about 2/3 Fe_2O_3 and 1/3 MnO_2), Harrison Meyer Black (An Fe-Co-Ni mixed oxide) and Columbian Mapico Black (a synthetic magnetite of about 22% FeO and 77% Fe_2O_3).

As compounds of the type (e) there may be especially mentioned, for example, MoS_2 , $MoSe_2$, $MoTe_2$, WS_2 , MnO_2 , FeS_2 , SnO_2 and CrO_2 .

Examples of preferred fillers are mixtures of the following:—

stoichiometric or non-stoichiometric Fe_3O_4 with one or more of the compounds specified in groups (a) to (g) above, for example a mixture of Co_3O_4 and stoichiometric or non-stoichiometric Fe_3O_4 , $Fe_2O_3 \cdot 0.8 FeO$ with MoS_2 , a carbon black or barium titanate; MoS_2 with one or more of the compounds specified in groups (a) to (g) above and $Fe_2O_3 \cdot 0.8 FeO$ with a metal powder.

Si_3N_4 and $CoAl_2O_4$ mentioned above are preferably used in admixture with a particulate, conductive filler.

As conductive particulate fillers there may be mentioned for example, carbon blacks, metallic powders, for example aluminium, chromium, copper, bronze, brass, iron, stainless steel, lead, silver, manganese, zinc, Ni/Al and nickel powders, and particulate platinized — or palladized-asbestos, -silica, -alumina, and -charcoal.

The compounds may also be used in admixture with silicon carbide particles.

The proportion of particulate compounds and fillers may be widely varied, depending on a) the electrical properties required of the material, b) the chemical nature of the compound and filler and c) the chemical nature of the polymer. The desired proportion may be determined relatively simply by experimentation. In general, the particulate compound will be present to at least 10% by weight of the polymer and more particularly the weight ratio of particulate compound to polymer will be within the range of from 100 to 500:100. The conductive particulate filler will generally be used in a concentration up to a maximum of 40 parts in the case of carbon black and of 100 parts in the case of metal powders relative to 100 parts by weight of polymer provided that γ is always at least 1.5. Typical values for the conductive particulate filler are in the region 10—25 parts (carbon black) and 50 to 100 (metal powder) per 100 parts of polymer.

The particle sizes of the particulate compounds are preferably below 20μ , more preferably below 5μ . Especially if the material is to be processed into a heat-shrinkable article, as described hereinafter, generally the smaller the particle size the better are the physical properties of the article.

The basic polymeric material comprises a polymer, especially an elastomer, containing units derived at least from ethylene and propylene. Examples of such polymers are copolymers containing only units derived from ethylene and propylene (e.g. the so called ethylene/propylene rubbers) and ethylene/propylene/non-conjugated diene terpolymers. Blends of such polymers with one or more other polymers may be desirable in some cases and the polymers selected will depend at least to a certain extent on the purpose to which the material is to be put. Examples of suitable polymers that may be blended with the basic polymer are as follows:

Polyolefins, including copolymers of ethylene with propylene, butene, methylacrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, vinyl acetate, vinyl chloride, vinyl propionate, carbon monoxide, maleate, fumarate and itaconic esters, terpolymers of ethylene, vinyl acetate and olefinic unsaturated monocarboxylic acid

such as acrylic or methacrylic acid. The partially neutralized varieties of these polymers such as the ionomeric resins which are the ammonium or alkali or alkaline earth metal derivatives: polyvinyl chloride, vinyl chloride copolymers containing as comonomer, vinyl acetate, vinylidene fluoride, dialkyl maleate, or fumarate, natural rubber, synthetic rubbers such as butyl, neoprene, silicone rubbers, including those derived from dimethyl siloxane, diphenyl siloxane, methylphenyl siloxane or methyl phenyl vinyl siloxane or the so-called mono methyl resins such as the Dow Corning 96083, copolymers of siloxanes with carboranes as in the Dexsil series of resins, or copolymers of siloxanes with styrenes; fluoro carbon plastics and rubbers including polyvinylidene fluoride, copolymers of vinylidene fluoride and hexafluoropropylene, terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, copolymers of vinylidene fluoride and 1-hydropentafluoro propene or a terpolymer containing these monomers plus tetrafluoroethylene, nitrile rubbers, acrylate rubbers, and polysulphide rubbers.

In addition, chemically modified versions of these or other polymers are also eminently suitable, for example, chlorinated polyethylene, chlorosulphonated polyethylene (Hypalon (Registered Trade Mark)), chlorinated rubber. Other suitable polymers include polyurethane elastomers and plastics, polyesters such as the Hytrel (Registered Trade Mark) rubbers from Du Pont, polyethers, epichlorohydrin rubbers, epoxy resins, dodecamethylene polypyromellitimide, block copolymers such as the Kraton rubbers which are styrene, butadiene, styrene blocks or the analogous styrene isoprene, styrene blocks, are also suitable. In addition, polymers based on ethylene oxide are also suitable. These polymers may contain one or more conventionally used additives for example, processing aids, plasticizers, stabilizers, antioxidant coupling agents, further modified or unmodified fillers and/or cure systems.

The materials may be manufactured by normal compounding methods, for example using internal mixers of the Banbury type, compounding mixer extruders, twin-roll mills, or high speed solvent mixers of the Silverson type of Sigma-bladed solvent mixers of the Baker Perkins type.

The material may be in the form of a shaped article, for example in the form of a tape, film, extruded tubing or moulded article or in the form of a dispersion or solution thereof in a liquid, for example as a paint or varnish which paint or varnish which will, on drying, leave a coating of the material on the equipment to which the paint or varnish has been applied. Preferably an article comprising a material of the invention is capable of changing shape when heated. The article, for example extruded tubing, may be mechanically shrinkable and in such a case the article will have to be of a resilient material. A preferred mechanically shrinkable article comprises for example, tubing maintained in a radially extended state by an internally disposed spiral of a stiff member; removal of the member causing the tubing to return to the original size and shape whereby it may be recovered onto an electrical apparatus.

Mechanically extendable articles may be extended immediately prior to application thereof to electrical apparatus using, for example, pliers or forceps.

In all cases the polymeric material is preferably crosslinked. More preferably the article is heat recoverable or is capable of being rendered heat recoverable or is dimensionally unstable. In such a case the article will generally be extruded tubing, extruded tape or a moulded component.

By the term heat "recoverable article", there is meant an article which retains its dimensions under low or normal temperature conditions, but at least one dimension of which is reduced upon heating to a critical temperature.

If the article is to be heat-shrinkable, the article is preferably made of suitable cross-linked or cross-linkable polymer. Especially suitable polymers are those heat-shrinkable polymers or polymer combinations described in British Patent Specifications Nos. 1 433 129, 1 294 665 and 1 434 719. The article may be rendered heat shrinkable by conventional methods, thus the material construction is firstly fabricated and is then cross linked, for example by irradiation with β or γ irradiation or by chemical means. The article is then expanded by the desired amount at a temperature at or above the said critical temperature and the article is then cooled to a temperature below said critical temperature while maintaining it in the expanded state. The articles have, for example, the following applications:

(i) Insulation for electric cables, where this insulation is situated between the conductor and the primary dielectric or between the screen of the cable and the primary dielectric. In the latter case an especially advantageous situation arises, in that the high voltage cable does not need a normal termination.

(ii) Insulation for electric cables as in the layered construction described in U.S. Patent No. 3,666,876.

(iii) Stress control coverings for electrical cable terminations. Such stress control means may be in the form of coatings, moulded parts, tubing or tape and may be used with or without an external protective layer, as necessary.

(iv) Stress control coverings for stator-bar ends or the ends of insulated electrical conductors in machines.

(v) Stress control components in lightning arrestors.

(vi) Attachments to aircraft wings to dissipate static.

(vii) As components of insulator bodies where the material may be the outer layer or an internal component, provided that it is non-tracking in service; thus it could be used for sheds or tubing to provide insulators for tension suspension, post or brushing insulators.

(viii) Electric switches or gates, i.e. an electrical device which remains insulating until a critical electrical stress is applied across it, whereupon the device undergoes a major increase in conductivity.

(ix) As components of carbon-black loaded polymeric conductive compositions to prevent local overheating caused by variations in composition or manufacturing techniques. Such compositions form the heating element of a linear heating strip having a pair of longitudinal electrodes, one at each edge of the strip; if a longitudinal strip between the electrodes has a higher resistance than the remainder it tends to overheat; the higher stress caused by the higher resistance portion results, however, in a higher conductivity of the materials of the invention, thus giving some degree of negative feedback.

The following Examples 1 to 3, 5 to 74, 77 to 82, 86 to 88, 91, 96 to 98, 103 to 108 and 110 to 133 illustrate the invention.

The graphs, circuit diagrams and cable terminations referred to in the Examples are shown in Figs. 1 to 31 of the accompanying drawings.

Example 1.

The following substances were mixed together in a twin roll laboratory mill at about 110°C.

Parts by weight

Royalene 611 (an ethylene-propylene-ethylidene norbornene (ENB) terpolymer containing about 70% ethylene and 35% ENB and having a Mooney viscosity of about 60. It is oil extended with 40 parts per hundred of paraffinic oil)

60

DYNH (a low density polyethylene of melt flow index 3 — Union Carbide)

16

DPD 6169 (an ethylene-ethyl acrylate copolymer of melt flow index 4 containing about 80% ethyl acrylate)

24

Agerite Rosin D (an antioxidant comprising polymerised trimethyl-dihydroquinoline)

3.3

Zinc Stearate

2

Triallyl Cyanurate

1.5

Black Iron Oxide (non-stoichiometric Fe_3O_4) (FW 17134)

300

The resultant material was granulated and extruded in the form of tubing having an internal diameter of 1.14 cm a wall thickness of 0.23 cm.

The tubing was then cross-linked by irradiating it with γ -rays from a U^{235} Spent fuel Source (0.8 MeV Energy).

Certain physical properties of the resultant cross-linked tubing were measured and found to be as follows:

	at 23°C	at 150°C
Tensile Strength	61 Kg/cm ²	14 Kg/cm ²
Elongation at break	213%	404%
100% modulus (H ₁₀₀)	—	6 Kg/cm ²

The tubing was then expanded, 150°C., in a standard Raychem expander to an internal diameter of 2.54 cm.

Its electrical properties were measured as described in Fig. 25 of the accompanying drawings which show a sectional side elevation of one end of a 11.6/20 kilovolt cable which has been prepared for termination.

Referring to Fig. 25 of the drawings, a 11.6/20 kilovolt polyethylene cable designated generally by reference numeral 1 comprises a central conductor 2 surrounded by a conducting polyethylene stress control layer 3, the layer 3 being surrounded by an insulating layer 4. The bulk portion of the cable 1 also comprises a carbon paper layer 5, a copper screen 6 and an outer insulating sheath 7. The terminated portion of the cable 1 comprises the central conductor 2, the conducting polyethylene stress control layer 3, the insulating layer 4 and a short length of the carbon paper layer 5 and copper screen 6 extending from the bulk portion of the cable. The end of the cable 1 is provided with a cable lug 8 attached to the control conductor 2.

An 8 cm length of the expanded tubing was shrunk on to the terminated portion of the cable 1 with an overlap of about 2 cm on to the extended portion of the copper screen 6, to provide a stress control covering 9. The heat-shrinkable tubing was also shrunk on to whipping 10 and an earth tail 11 within the region of overlap on to the copper screen 6. No attempt was made to fill the air gap between the covering 9 and the extended portion of the copper screen 6.

The discharge magnitude of a 2 cm length of the above 11.6/20 kilovolt cable, each end of which had been terminated as described above was determined using the apparatus and circuit shown in Fig. 26 of the accompanying drawings.

Referring to Fig. 26 of the drawings an earthed wire screen cage 12 contains a discharge-free step-up transformer 13, the secondary windings of which are connected to the central conductor 2 and the screen 6 respectively of the cable 1, through earth, via a parallel-connected voltage dropper 14 and blocking capacitor 15. The primary windings of the transformer 13 are connected to an AC input via a control and filter unit 16. Discharge levels in the cable and end terminations were measured using an ERA Mark III discharge detector 17 connected as shown.

The results were as follows:

	Discharge Magnitude (pC)	Applied Voltage (kV r.m.s.)
	1	33 kV
	5	41 kV

For comparison the same cable, in the absence of the shrunk tubing at the terminations, was tested in the same manner. Discharges of 5 pC at an applied voltage of 4.8 kV r.m.s. were obtained.

It may thus be seen that the tubing of the material of the invention gave excellent stress control and that the cable was discharge free at the normal working voltage (11.6 kV r.m.s phase to ground).

The resistance characteristics of the material were measured in the following manner:

A plaque measuring 15.3 cm×15.3 cm×0.1 cm of the material was placed between two brass electrodes manufactured to the dimensions given in BS 2782 pt. 201C, 1970, page 110.

The current flowing between the brass electrodes was measured as a function of D.C. voltage between 100 V and 10 kV, using the circuit shown in Fig. 1 of the accompanying drawings.

The current I and voltage V were found to be related by the equation.

$$I = KV^{\gamma}$$

where

I is current

V is applied voltage

K is a constant, and

for a linear material i.e. on which obeys

Ohm's Law, $\gamma = 1$.

For the material of this example γ was found to be 3.0. At a voltage stress of 1kV/mm the plaque passed a current of 96 μ A.

Example 2.

The following substances were mixed together, at about 110°C in a twin roll laboratory mill:

		Parts by weight	
15	Royalene 611	60	15
	DYNH	16	
	DPD 6169	24	
	Agerite Resin D	3.3	
	Zinc Stearate	2	
20	Cobalt Oxide (Co_3O_4)	300	20
	Triallyl Cyanurate	1.3	
	$\alpha\alpha'$ -bis (t-butylperoxy)		
	m-p di-isopropyl benzene	5	

A plaque 1 mm thick was moulded from the resultant material at 190°C for 10 mins. and its resistance characteristics were determined as described in Example 1. The value of γ was 2.85 and the current passed by the plaque at a stress of 1kV/mm was 285 μ A.

Raychem Parts No. RUK 453—3 (tubes of 100 mm length, 3 mm wall thickness, unexpanded internal diameter 20 mm, expanded diameter 40 mm) were moulded from the material and the stress-grading properties of the material were tested by the method described in Example 1 using a terminated 2 metre length of 5.8/10kV cable having such a part shrunk on to each termination.

The discharge levels obtained were:

	Discharge Magnitude pC	Applied Voltage kV/r.m.s.	
35	1	20	35
	5	25	

The discharge magnitude for the cable in the absence of stress grading means was 5pC at 4.8kV.

It can thus be seen that this material has good stress grading properties.

Example 3.

The following substances were mixed together at about 110°C in a twin roll laboratory mill:

		Parts by weight	
45	Royalene 301T (a 65% by weight ethylene/35% by weight propylene copolymer having a Mooney viscosity of 60)	60	45
	DPD 6169	16	
	DYNH	24	
	Strontium Titanate	367	
50	Agerite Resin D.	4	50
	Triallyl Cyanurate	2	
	2,5 dimethyl-2,5 di-t-butyl peroxyhexyne-3	4	

A plaque 1 mm thick was moulded from the resultant material and the resistance characteristics were determined by the method described in Example 1.
 γ was found to be 2.55 and the current passed by the plaque at a stress of 1kV/mm was 0.3 μ A.

5

Example 5.

5

The following substances were mixed together at about 110°C in a twin roll mill.

		Parts by weight	
10	Royalene 301T	60	
	DPD 6169	16	10
	DYNH	24	
	Barium Titanate	376	
15	Vulcan (Registered Trade Mark) XXX Special (an oil furnace carbon black having a particle size of 20.25 $m\mu$)	10	15
	Agerite Resin D	4	
	Triallyl Cyanurate	2	
	Dicumyl Peroxide (40%)	4	

A plaque 1mm. thick was moulded from the resultant material at 178° and its resistance characteristics were determined as described in Example 1.
 γ was found to be 1.80 and the current passed by the sample at a stress of 1kV/mm and 0.81 μ A.

20

20

For comparison a similar material without Vulcan XXX Special which is a conductive carbon black, gave a γ value of 3.40 and the current passed at a stress of 1kV/mm and 0.031 μ A.

25

25

EXAMPLES 6-11

The following substances were mixed together in a twin roll laboratory mill.

Example No.	6	7	8	9	10	11
Royalene 611	60	60	60	60	60	60
DYNH	16	16	16	16	16	16
DPD 6169	24	24	24	24	24	24
Agerite Resin D	4	4	4	4	4	4
Zinc Stearate	2	2	2	2	2	2
Triallyl cyanurate	1.5	1.5	1.5	1.5	1.5	1.5
MoS ₂	300	200	—	—	—	—
MoTe ₂	—	—	300	200	—	—
MoSe ₂	—	—	—	—	300	200

Each material was then pressed at 130°C into a plaque 150 × 150 × 1mm., and the resistance characteristics were determined as described in Example 1.

30

Graphs of log I vs. log V for the plaques of these Examples are shown in Figs. 2 to 4 of the accompanying drawings.

30

The values of γ were determined to be as follows:

Example No.		γ	
5	6	3.3	
	7	3.8	
	8	(low stress) $V_r=5.0$	
	9	(high stress) $V_s=2.0$	(see graph)
	10	2.6	
	11	4.5	
		10	

10 Graphs of current vs. voltage for Examples 6 and 7 are shown also in graphs 45 and 44 respectively of the accompanying drawings. 10

In the remaining Examples the following base polymer was used unless stated otherwise.

Examples 12 to 45.
Mixtures of Spinel and Conductive Metallic Particles

	Parts by weight	
15	Royalene 611	60
	DYNH	16
	DPD 6169	24
	Agerite Resin D.	4
	Zinc Stearate	4
20	Triallyl cyanurate	1.5

25 200 parts by weight of Fe_3O_4 supplied by Pfizers Limited under the trade name BK 5099 (a particularly pure product of the formula $Fe_2O_3 \cdot 0.8 FeO$ containing from 25.4 to 25.6% FeO and 72.5 to 73.5 FeO_3) or 200 parts by weight of CO_3O_4 supplied by Hopkins and Williams were added to the base polymer. Additional metal fillers were added in the amounts shown in Tables 1 and 11 which follow. The ingredients were processed as described in the earlier Examples and slabs $150 \times 150 \times 1mm$ were prepared as previously described. The current-voltage characteristics were determined as described previously. 25

30 The γ values obtained are given in Tables 1 and 11 and the current-voltage graphs are shown in graphs 1—30 of the accompanying drawings. 30

TABLE 1 — Fe_3O_4

Example No.	Metal and loading	γ	Graph No.
12	50 pts Al	5	1
13	100 pts Al	Sample punctured at 40 volts	—
14	50 pts Cu	14.3	2
15	100 pts Cu	16.4	3
16	50 pts Fe	5.1	4
17	100 pts Fe	10.4	5
18	50 pts Mn	4.4	6
19	100 pts Mn	9.6	7
20	100 pts Cr	3.5	8
21	100 pts Pb	8.75	9
22	50 pts Ni	2.6	10
23	100 pts Ni	2.9	11
24	50 pts Ni/Al	12	12
25	100 pts Ni/Al	Sample punctured at 50 volts	—
26	50 pts Zn	7.75	13
27	100 pts Zn	8.8	14
28	50 pts Ag	17	15
29	100 pts Ag	Sample punctured at 100 volts	—

Where the sample is indicated to have punctured, this means that, at the stated stress, the sample was so conductive that it shorted out. The Ni/Al in Examples 41 and 42 was based on Raney Nickel powder.

TABLE II - Co_3O_4

Example No.	Metal and loading	γ	Graph No.
30	50 pts Al	7	16
31	100 pts Al	8	17
32	50 pts Cu	5.6	18
33	100 pts Cu	5.8	19
34	50 pts Fe	4.1	20
35	100 pts Fe	3	21
36	50 pts Mn	5.75	22
37	100 pts Mn	6.3	23
38	100 pts Pb	7.25	24
39	50 pts Ni	16.6	25
40	100 pts Ni	12.3	26
41	50 pts Ni/Al	21	27
42	100 pts Ni/Al	Sample punctured at 2KV	—
43	50 pts Zn	3.8	28
44	100 pts Zn	10	29
45	50 pts Ag	5	30

5

These results show that all the compositions exhibited non linear behaviour.

5

Examples 46 to 51.

Mixtures containing Carbon Blacks

5 Various amounts of Vulcan XXX Special, a conductive black made by Cabot Carbons, were blended with Fe_3O_4 (BK 5099) and Silicon Nitride (supplied by Advanced Materials Engineering Limited). The voltage current characteristics were measured as before and the results are shown in Table III and in graphs 31 to 36 of the accompanying drawings. In Table III and the following tables "phr" means parts, by weight, per hundred parts of polymer base.

These results show that all the mixtures behaved in a non linear fashion.

TABLE III

Example No.	Fillers and Loading	γ	Graph No.
46	33 phr Fe_3O_4 , 13.3 phr XXX Sp.	5.03	31
47	100 phr Fe_3O_4 ,	5.08	32
48	300 phr Fe_3O_4 ,	1.7	33
49	300 phr Fe_3O_4 , 16.7 phr XXX Sp.	1.55	34
50	300 phr Fe_3O_4 , 20.0 phr XXX Sp.	1.64	35
51	200 phr Si_3N_4 , 20	4	36

Examples 53 to 58.

Mixtures of Fe_3O_4 and barium titanate

15 Various mixtures, as shown in Table IV, were added to the base polymer. The voltage-current characteristics were determined as described earlier. The γ values obtained are given in Table IV and voltage-current graphs are shown in graphs 38 to 43 of the accompanying drawings. These results show that the materials behave in a pronounced non-linear fashion.

TABLE IV

BaTiO₃/Fe₃O₄ (BK 5099)

Example No.	Fillers and Loading	γ	Graph No.
53	200 phr Fe_3O_4 , 100 phr BaTiO ₃	10	38
54	250 phr Fe_3O_4 , 50 phr BaTiO ₃	5.1	39
55	150 phr Fe_3O_4 , 150 phr BaTiO ₃	6.6	40
56	100 phr Fe_3O_4 , 200 phr BaTiO ₃	3	41
57	150 phr Fe_3O_4 , 75 phr BaTiO ₃	12.7	42
58	100 phr Fe_3O_4 , 50 phr BaTiO ₃	4.3	43

TABLE V
MoS₂ and Mixtures using it

The following fillers were added to the polymer base and the voltage-current characteristics determined as described above.

Example No.	Fillers and Loading	γ	Graph No.
59	200 phr MoS ₂	3.8	44
60	300 phr MoS ₂	3.3	45
61	300 phr Fe ₃ O ₄ + 5 phr MoS ₂	3.75	46

Other Fillers

Results using other suitable fillers are given in Table VI and graphs 47 to 58. The fillers were added to the polymer base and the voltage-current characteristics determined as described above.

5

5

TABLE VI
Miscellaneous Fillers

Example No.	Filler Loading	γ	Graph No.
	<u>Fast Black 100</u>		
	(50% Cr ₂ O ₃ , 40% Fe ₂ O ₃ , 10% CuO)		
62	300 phr	6.8	47
63	400 phr	8.3	48
	<u>Copper Chromite</u>		
64	300 phr	1.6/3.8	49
	<u>Cobalt Ferrite</u>		
65	300 phr	4.9	50
	<u>Manganese Tetroxide</u>		
66	300 phr (99.9% purity)	2.1	51
67	300 phr (90% purity)	1/1.75	52
68	200 phr (90% purity)	1.75	53
	Impurity unknown, possibly MnO ₂		
	<u>Copper Manganite</u>		
69	300 phr	1.3/2.0	54
70	200 phr	1.5	55
71	150 phr	7.2	56
72	100 phr	12	57
73	190 phr	4.1	58

Effect of polymer Base

It has been noted that the base polymer has a large effect on the non-linear behaviour of a given system and this is probably due to contributions of the polarity of the polymer and/or contributions from catalyst residues. The effects of using different polymers with a given filler were determined and the results are given in Tables VII, VIII and IX and in graphs 59 to 87.

5

5

TABLE VII

Filler: FW 17134. All 300 phr on 100 phr polymer.

Example No.	Polymer	γ	Graph No.
77	Royalene 502	10	62
78	Royalene 611	8	63
79	Royalene 512	7.5	64
80	Royalene 301T	10	65
81	Royalene 1812	6	66
82	Royalene 400	9	67

TABLE VIII

Filler: BK 5099. All 300 phr on 100 phr polymer.

Example No.	Polymer	γ	Graph No.
86	Royalene 611	15	71
87	Royalene 512	15.6	72
88	Royalene 1812	6.8	73
91	Royalene 400	6	76

TABLE IX

Co₃O₄. All 300 phr on 100 phr polymer.

Example No.	Polymer	γ	Graph No.
96	Royalene 611	7	81
97	Royalene 1812	10	82
98	Royalene 512	10.2	83

The FW17134 referred to in Table VII is a natural ground magnetic iron oxide and is available as a pigment from Ferro Limited.

Effect of Fe_3O_4 from different suppliers

In addition to observing differences in behaviour of the fillers with different base polymers, it has been found that nominally identical fillers from different suppliers also show very large variations in properties when mixed in the same base polymer. This effect is very well illustrated in Table X and graphs 88 to 95, which show variations using Fe_3O_4 from a variety of suppliers.

The base polymer had the following composition:

	Parts by weight	
Royalene 611	60	
DYNH	16	
DPD 6169	24	
Agerite Resin D	4	
Filler	300	
Zinc Stearate	4	
Triallyl cyanurate	1.5	

TABLE X

Example No.	Supplier	Filler	γ	Graph No.
103	Ferro	FW 17134	3	88
104	Columbian Carbon Co.	Mapico Black	5.5/2.25	89
105	Pfizer	BK 5099	5.3	90
106	Pfizer	MO-4232	2	91
107	Pfizer	MO-8029	7.2	92
108	Ferro	FW 1790	4.5	93
109	Hopkins and Williams	Precipitated Fe_3O_4	1.3	94*
110	Bayer	303 T	6.2	95

* Comparison Example — Sample blew up at 800v i.e. puncture occurred.

All formulations are shown to be non-linear but the degree of non-linearity varies widely between 1.3 and 7.2.

The reason for these differences probably lies in the fact that the method of manufacture is primarily designed to produce a pigmentary product rather than a pure chemical.

Concentration Effects

The degree of non-linearity varies also with the amount of filler loaded into the base polymer of this effect was demonstrated for several materials. Table XI and graphs 96 to 102 give data for two different types of Fe_3O_4 , namely, FW 17134 and BK 5099.

TABLE XI

Example No.	Filler Loading	γ	Graph No.
	<u>FW 17134</u>		
111	300 phr	3	96
112	200 phr	5.9	97
113	100 phr	4.1	98
114	250 phr	5.9	99
	<u>BK 5099</u>		
115	300 phr	5.3	100
116	250 phr	7	101
117	200 phr	9	102

The data shows that the degree of non-linearity can be varied between 3 and 5.9 in the case of FW 17134 and 5.3 and 9 in the case of BK 5099. This type of variation may be regarded as typical for the effects of different loadings.

5 Magnesium and Zinc Ferrites

Magnesium and zinc ferrites supplied by the Columbian Carbon Company were loaded into the polymer base given below and the results are given in Table XII and in graphs 103 to 106.

	Polymer base	Parts by weight
10	Royalene 611	60
	DYNH	16
	DPD 6169	24
	Agerite Resin D	4
	Triallyl cyanurate	15

TABLE XII

Example No.	Loading	Filler	γ	Graph No.
118	300 phr	Mg Ferrite	2.8	103
119	200 phr	Mg Ferrite	3.9	104
120	300 phr	Zn Ferrite	1.79	105
121	200 phr	Zn Ferrite	4.17	106

These results show the materials to be non-linear.

Mixtures of Fe_2O_3 and Co_2O_3

Mixtures of Fe_2O_3 and Co_2O_3 were loaded into the following polymer base.

		Parts by weight	
5	Royalene 611	60	
	DYNH	16	5
	DPD 6169	24	
	Agerite Resin D	4	
	Zinc Stearate	4	
	Triallyl cyanurate	1.5	

10 The results are shown in Table XIII, and in graphs 107 to 116.

10

TABLE XIII

Example No.	phr BK 5099	phr Co_2O_3	γ	Graph No.
122	270	30	5.6	107
123	240	60	6	108
124	210	90	5.5	109
125	180	120	7.2	110
126	120	180	6	111
127	90	210	5.4	112
128	60	240	5.2	113
129	30	210	5.4	114
130	150	150	7.6	115
131	0	300	4.45	116

Again all the materials exhibited marked non-linear behaviour.

Example 132.

15 The following material was compounded on a 40" twin roll mill at about 110°C:

15

		Parts by weight	
	Royalene 611	60	
	DYNH	16	
	DPD 6169	24	
20	Agerite Resin D	4	20
	Triallyl cyanurate	2	
	Zinc Stearate	4	
	BK 5099	300	
	Molybdenum disulphide	5	

25 The resulting material was granulated and extruded to produce a tube of the following dimensions:

25

Internal diameter	0.430 inches (1.08 cm)
Wall thickness	0.075 inches (0.17 cm)

The extrusion conditions, on a 2½ inch (6.3 cm) extruder, having an L/D ratio of 25:1 were:

Zone	1	2	3	4	5	Head 1	Head 2
Temperature °C	80	90	100	110	120	130	120

5 The tubing was then irradiated using 5.8 MeV electrons to a total dose of approximately 12.5 Mrads after which the tubing was found to have a 100% Modulus at 150°C of 4—6 Kg/cm². This material had a γ value of 5.0 and the full current-voltage stress plot is given in Figure 30. 5

10 This tubing after expansion to a diameter of 1 inch (2.54 cm) was used to terminate a number of high voltage power cables by heat shrinkage with a propane gas torch as outlined below: 10

a) 20 KV polyethylene insulated cable, type A2YHSY, 50 mm² conductor, of 5.6 mm insulation thickness. The detailed construction of this cable is shown in Fig. 27, in which the reference numerals have the following meanings:

15	281 PVC SHEATH	15
	282 WRAP of Mylar (Registered Trade Mark) or plain cloth	
	283 COPPER WIRE SCREEN with copper contact strip	
	284 SEMI-CONDUCTING LAYER (impregnated paper and cloth)	
	285 GRAPHITE COATING	
20	286 INSULATION (polyethylene, or cross linked polyethylene)	20
	287 STRESS RELIEF LAYER (conducting polyethylene or cross linked polyethylene)	
	288 CONDUCTOR	

25 The cable was terminated as illustrated in Fig. 28 of the accompanying drawings, wherein the layers of the construction are stripped as shown. A length of the tubing 289 was shrunk over the stripped cable, extending over 23 cm of the insulating layer 286, and overlapping on to the layer 282. The cable was then tested as illustrated in Fig. 26 of the accompanying drawings, with the following results: 25

	Discharge magnitude	Applied Voltage	
	pC	(kV r.m.s.)	
30			30
	Initially	50	
	After 21 days heat cycling	27	

35 The heat cycling was carried out, using a continuously applied voltage of 40 KV, and passing current such that the sheath of the cable reached 70°C for 6 hours, followed by cooling to ambient temperature for 6 hours and then reheating the cable for a further period of 6 hours etc. 35

The impulse strength of the termination was determined in accordance with B.S. 923 with the following results:

	Impulse Strength KV	
40		40
	Initially	135
	After 21 days heat cycling	>200

These results taken together indicate the good stress control provided by the tubing made according to the invention.

45 b) 10kV PVC insulated cable, 50 mm² conductor, 3 mm insulation thickness. The construction of this cable is as shown in Fig. 27 of the accompanying drawings, except that the layer 284 is simply impregnated paper and layers 286 and 287 are polyvinyl chloride rather than polyethylene. 45

Using an 8 cm. length of the tubing according to the invention and covering

with a non-tracking heat shrinkable tubing 290 made according to Example 8, sample No. 44 of British Patent 1,337,951, the regions below the ends of the tubing being covered with a sealant (not shown), the following results were obtained:

	Discharge Magnitude, pC	Applied Voltage (kV r.m.s.)	
5	0.3	22.5	5
	0.6	29	
	0.6	37	
	0.6	50	

The impulse strength determined to BS 923 was found to be 105kV.

10 This example demonstrates the good stress control afforded by the tubing, even at a voltage 9 times that at which the cable normally operates (5.8 kV r.m.s.). 10

Further experiments were carried out on a similar loop of cable, without the outer layer of non-tracking tubing, to determine the effect of length of the stress control layer.

15 The results were as follows: 15

	Effective length of stress control tubing, cm	Applied Voltage required for 5pC max discharge	
	1	7	
	2	16	
20	5	27	20
	10	30	
	20	31	
	25	31	

25 c) 25 kV XLPE 2/0 conductor size concentric neutral cable, with extruded screen as shown in Fig. 29, in which the reference numerals have the following meanings: 25

- | | | |
|-----|-------------------------------------|----|
| 301 | SCREEN of thick tinned copper wire: | |
| 302 | EXTRUDED CONDUCTING XLPE LAYER | |
| 303 | INSULATION XLPE | |
| 304 | STRESS RELIEF LAYER (conducting PE) | 30 |
| 305 | CONDUCTOR | |

Using a conductive paint over 2 cm of dielectric from the end of the screen (of volume resistivity approx. 10 Ω cm.) and a 25 cm. length of the above stress control tubing, the following results were obtained:

	Discharge magnitude	Applied Voltage	
	pC	kV r.m.s.	
a) before heat cycling	0	25	
	0.3	33.5	
40	0.3	40	
	0.6	45	
	2	50	40
b) after heat cycling	0	25	
	2.5	35	
	2.5	40	
45	5.5	45	45
	10	50	

The heat cycling consisted of 18 cycles each of 4 hrs. heating to 65°C on the screen of the cable, +4 hrs. cooling to ambient and during the total cycling period a voltage of 20 kV r.m.s. was applied.

50 These results further illustrate the good stress control provided by the tubing of the invention. 50

Example 133.

The following formulation was compounded as already described:

		Parts by weight	
5	Royalene 611	60	5
	DYNH	16	
	DPD 6169	24	
	Agerite Resin D	4	
	Triallyl cyanurate	2	
10	Zinc Stearate	4	10
	BK 5099	300	
	Vulcan XXX Special	5	

This material was processed into heat shrinkable tubing in the manner already described. The tubing so produced had an internal diameter of 1.75 cm and a wall thickness of 0.26 cm. It was expanded to an internal diameter of 4.32 cm.

15 This material had a γ value of 3.7 and the current voltage stress plot is given in Figure 30. 15

20 The tubing was used to terminate a 20 kV XLPE cable, construction as per Figure 28 and having a conductor cross sectional area of 150 mm². The cable designation was A2XH5Y. The insulation thickness was 5.6 mm and the cable termination was in accordance with Fig. 28, the effective length of the stress control layer being 23 cms. 20

25 The cable termination was heat cycled for 6 days at a continuous voltage of 40 KV, to 90°C on the cable jacket for 2½ hours, followed by cooling to ambient temperature for 2½ hours. 25

The principal electrical properties of the termination were:

	Discharge Magnitude pC	Applied Voltage kV r.m.s.	Impulse Strength kV
Initially	5	23	160
After heat cycling	5	24	190

These results show the good stress control provided by the tubing.

30 This tubing was further evaluated on a 20 kV XLPE cable, of conductor size 35 mm² and insulation thickness 5.6 mm. The construction of this cable is given in Fig. 31 of the accompanying drawings in which the reference numerals have the following meanings: 30

321 SHEATH (PVC)
322 COPPER TAPE SCREEN
323 SEMICONDUCTOR LAYER (Conducting XLPE)
324 INSULATION XLPE
325 STRESS RELIEF LAYER (Conducting XLPE)
326 CONDUCTOR 35

40 It was terminated as shown in Fig. 28 of the accompanying drawings using a total termination length of 330 mm and an effective length of the stress grading layer of 230 mms. 40

The discharge levels were measured before and after impulse testing and were found to be as follows:

		Discharge Magnitude pC	Applied Voltage kV r.m.s.	
45	Initially	0	30	45
		1	37	
	After Impulse testing	0	29	
		1	35	

The impulse testing consisted of 5 pulses of positive polarity only at each of the following voltages: 100, 110, 125, 140, 150, 160, 170, 180, 190 and 200 kV. No flashover occurred and the testing was discontinued after reaching 200 kV.

These results show the good stress control properties conferred by the tubing made according to the invention, both as regards corona discharge and impulse strength.

In the above Tables, the various polymers and fillers designated by manufacturers' names and codes have the following compositions:

Royalene 502 is believed to be an ethylene-propylene copolymer having an ethylene content of about 60% and a propylene content of about 40%, a Mooney viscosity of 62 and an iodine number of 1.

Royalene 512 is believed to be an ethylene-propylene copolymer having an ethylene content of about 70% and a propylene content of about 30% and a Mooney viscosity of 90.

Royalene 1812 is believed to be an ethylene-propylene copolymer containing about 80% ethylene.

Royalene 400 is believed to be an ethylene-propylene copolymer having an ethylene content of about 65% and a propylene content of about 35% and is an oil-extended rubber.

MO 4232 and 8029 of Pfizer are magnetic iron oxides (non-stoichiometric Fe_3O_4) of spherical and irregular particle shape respectively.

FW 1790 and 17134 of Ferro Ltd. are ground, natural magnetic iron oxides containing, respectively, 24% FeO and 68% Fe_2O_3 and 26% FeO and 68% Fe_2O_3 , the balance being impurities.

303 T of Bayer is a mixed phase pigment ($2/3 \text{ Fe}_2\text{O}_3$ and $1/3 \text{ MnO}_2$) having a bixbyite structure.

Hopkins and Williams' precipitated Fe_3O_4 is stoichiometric Fe_3O_4 .

WHAT WE CLAIM IS:—

1. A material comprising a polymeric material containing at least units derived from ethylene and propylene, the polymeric material having dispersed therein at least one particulate filler selected from

(a) compounds having a perovskite type crystal structure;
(b) compounds having a spinel crystal structure, other than $\gamma\text{-Fe}_2\text{O}_3$ and spinel itself;

(c) compounds having an inverse spinel crystal structure;

(d) compounds having a mixed spinel crystal structure;

(e) dichalcogenides of transition metals and of tin;

(f) AgI , Prussian blue, Rochelle salt and other alkali metal tartrates, compounds of the formula XH_2YO_4 , wherein X is K, Rb or Cs and Y is P or As, ammonium fluoroberyllate, thiourea, ammonium sulphate and triglycine sulphate;

(g) Si_3N_4 .

the total weight of said filler being at least 10% based on the weight of the polymeric material and the material having a γ -value of at least 1.5 at least at some direct current (DC) electrical stress between 0.01 kV/mm and 10 kV/mm.

2. A material as claimed in claim 1 wherein the filler comprises stoichiometric or non-stoichiometric Fe_3O_4 .

3. A material as claimed in claim 2 wherein the filler comprises a mixture of Co_3O_4 and stoichiometric or non-stoichiometric Fe_3O_4 .

4. A material as claimed in claim 2 or claim 3 wherein the filler comprises $\text{Fe}_2\text{O}_3 \cdot 0.8 \text{ FeO}$.

5. A material as claimed in claim 2 wherein the filler comprises a mixture of $\text{Fe}_2\text{O}_3 \cdot 0.8 \text{ FeO}$ and barium titanate.

6. A material as claimed in claim 1 wherein the filler comprises a sintered blend of substantially 50% by weight Cr_2O_3 , 40% by weight Fe_2O_3 and 10% by weight CuO .

7. A material as claimed in claim 1 wherein the filler comprises a mixed oxide of Fe, Co and Ni.

8. A material as claimed in claim 1 wherein the filler comprises a synthetic magnetite comprising substantially 22% FeO and 77% Fe_2O_3 .

9. A material as claimed in claim 1 wherein the filler comprises molybdenum disulphide.

10. A material as claimed in claim 9 wherein the filler comprises a mixture of $\text{Fe}_2\text{O}_3 \cdot 0.8 \text{ FeO}$ in admixture with MoS_2 .

11. A material as claimed in claim 1 wherein the filler comprises copper maganite.
12. A material as claimed in claim 1 wherein the filler comprises cobalt ferrite.
13. A material as claimed in any one of claims 1 to 12 wherein the filler also
5 comprises one or more particulate electrically conductive fillers.
14. A material as claimed in claim 13 wherein the conductive filler is carbon black and the weight ratio of conductive filler to polymer is at most 40:100 or wherein the conductive filler is a metal powder and the said weight ratio is at most 100 to 100.
15. A material as claimed in claim 14 wherein the filler comprises a mixture of
10 Fe_2O_3 , 0.8 FeO and a metal powder.
16. A material as claimed in claim 14 wherein the filler comprises a mixture of Fe_2O_3 , 0.8 FeO and a carbon black.
17. A material as claimed in claim 13 or claim 14 wherein the conductive filler is aluminium powder.
18. A material as claimed in claim 1 wherein the filler is selected from:
15 a) compounds having a perovskite-type crystal structure other than titanates of strontium, magnesium, nickel and barium;
b) compounds having a spinel crystal structure selected from compounds of the general formula $\text{A}^{2+}\text{B}^{3+}_2\text{O}_4$ wherein A is Mg, Co, Cu, Zn or Cd and B is Al, Cr, Fe, Mn, Co or V provided that when A is Mg, B is not Al, when A is Cu B is not Cr and when A is Zn, B is not Fe, and compounds of the general formula $\text{A}^{3+}\text{B}^{2+}_2\text{O}_4$ wherein A is Ti or Sn and B is Zn, Co, Ni, Mn, Cr or Cd;
c) compounds having an inverse spinel structure, other than stoichiometric Fe_3O_4 but including non-stoichiometric variants thereof;
25 d) compounds having a mixed spinel crystal structure;
e) MoSe_2 , MoTe_2 , MnO_2 and SnO_2 ;
f) AgI, Prussian blue, Rochelle salt and other alkali metal tartrates, ammonium fluoroberyllate, throurea, triglycine sulphate ($(\text{CH}_2\text{NH}_2\text{COOH})_3\text{H}_2\text{SO}_4$), ammonium sulphate and compounds of the general formula XH_2YO_4 wherein X is K, Rb or Cs and Y is P or As;
30 g) Si_3N_4 ;
h) a mixture of non-stoichiometric or non-stoichiometric Fe_3O_4 and MoS_2 ;
i) a mixture of stoichiometric or nonstoichiometric Fe_3O_4 and barium titanate;
j) a mixture of stoichiometric or non-stoichiometric Fe_3O_4 and at least one
35 metallic powder selected from Fe, Al, Cu, Mn, Cr, Pb, Ni, Zn and Ag; and
k) a mixture of barium titanate and a carbon black; the total weight of the compound(s) in the filler being at least 10% based on the weight of the polymeric material and the material having a γ -value of at least 1.5 at least at some direct current (DC) electrical stress between 0.01 kV/mm and 10 kV/mm.
19. A material as claimed in any one of claims 1 to 18 wherein the particle size
40 of the compounds of said filler is less than 20μ .
20. A material as claimed in claim 19 wherein said particle size is less than 5μ .
21. A material as claimed in any one of claims 1 to 20 wherein the material has a value of 1.5 or more at a DC electrical stress within the range of 0.1 and 5kV/mm.
22. A material as claimed in any one of claims 1 to 21 wherein the polymeric
45 material is elastomeric.
23. A material as claimed in any one of claims 1 to 22 comprising a polymeric material containing units derived solely from ethylene or propylene.
24. A material as claimed in any one of claims 1 to 22 comprising a polymeric material which is a terpolymer of ethylene, propylene and a non-conjugated diene.
25. A material as claimed in claim 24 wherein said diene is ethylidene norbornene.
26. A material as claimed in any one of claims 1 to 21 wherein said polymeric material is blended with one or more other polymers.
27. A material as claimed in claim 26 wherein said polymeric material is blended
55 with one or more polymers selected from polyethylene, an ethylene/ethylacrylate copolymer, or ethylene/vinyl acetate copolymer and a chlorinated polyethylene.
28. A material as claimed in any one of claims 1 to 27 wherein the filler also comprises silicon carbide.
29. A material as claimed in claim 1 substantially as described in any one of Examples 1 to 3, 5 to 74, 77 to 82, 86 to 88, 91, 96 to 98, 103 to 108 and 110 to 131
60 herein.
30. A material as claimed in claim 1 substantially as described in either of Examples 132 and 133 herein.
31. A material as claimed in any one of claims 1 to 30 wherein the polymer is cross-linked.

32. A material as claimed in any one of claims 1 to 31 that can be processed into a recoverable article.

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FIG. 1.

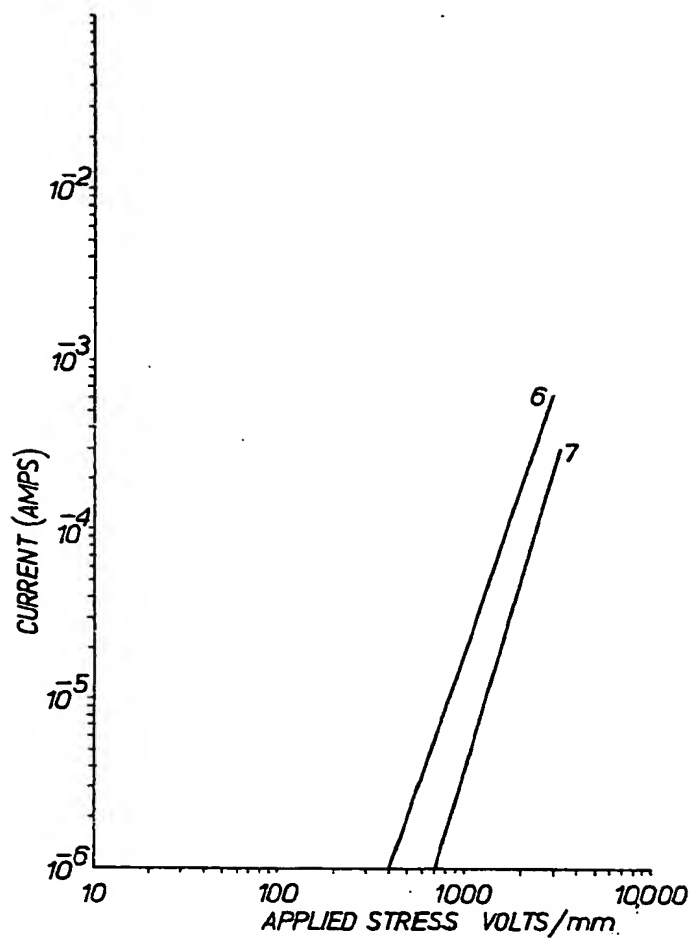


FIG.2.

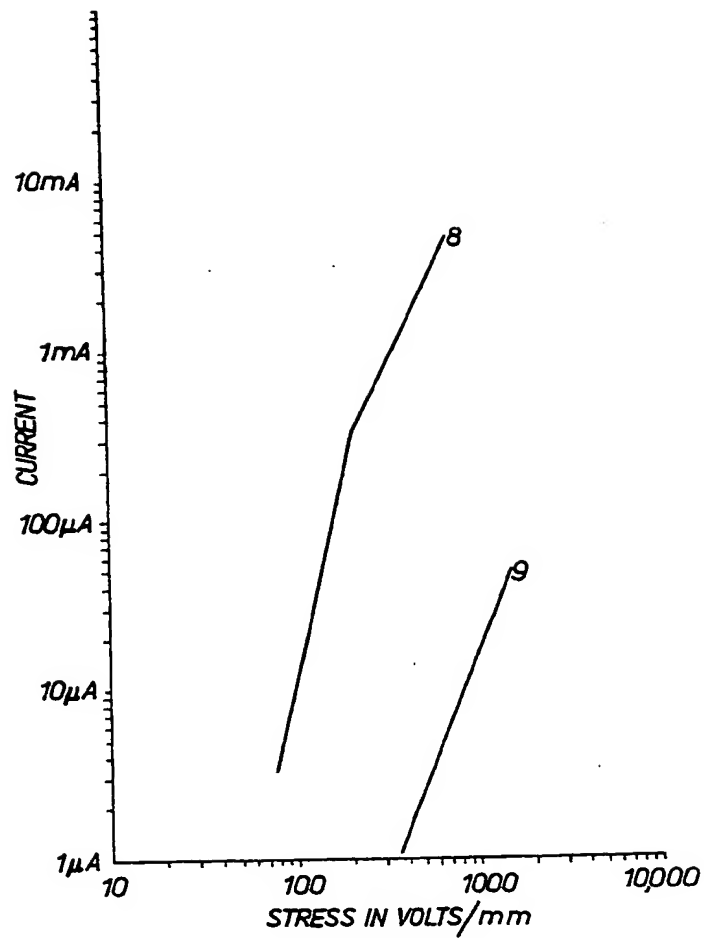
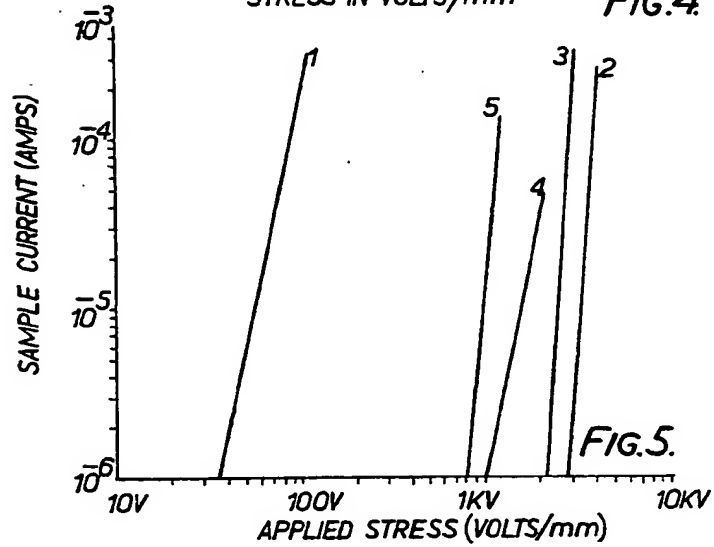
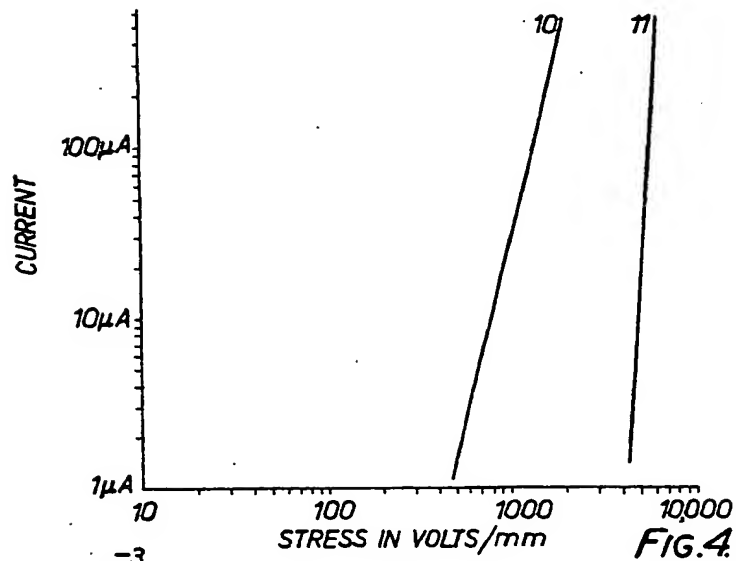


FIG. 3.



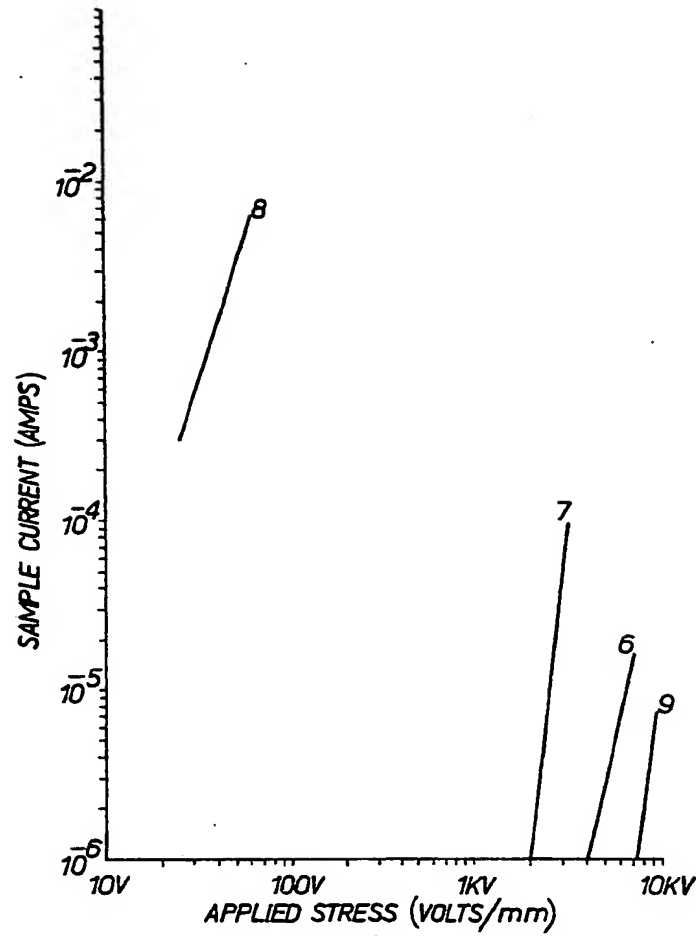


FIG. 6.

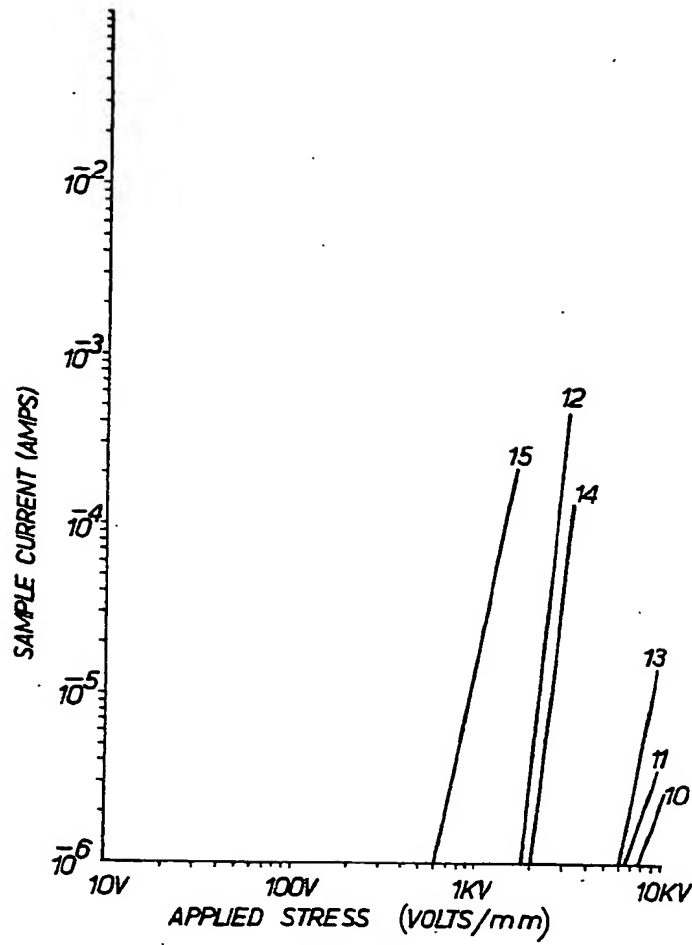


FIG. 7.

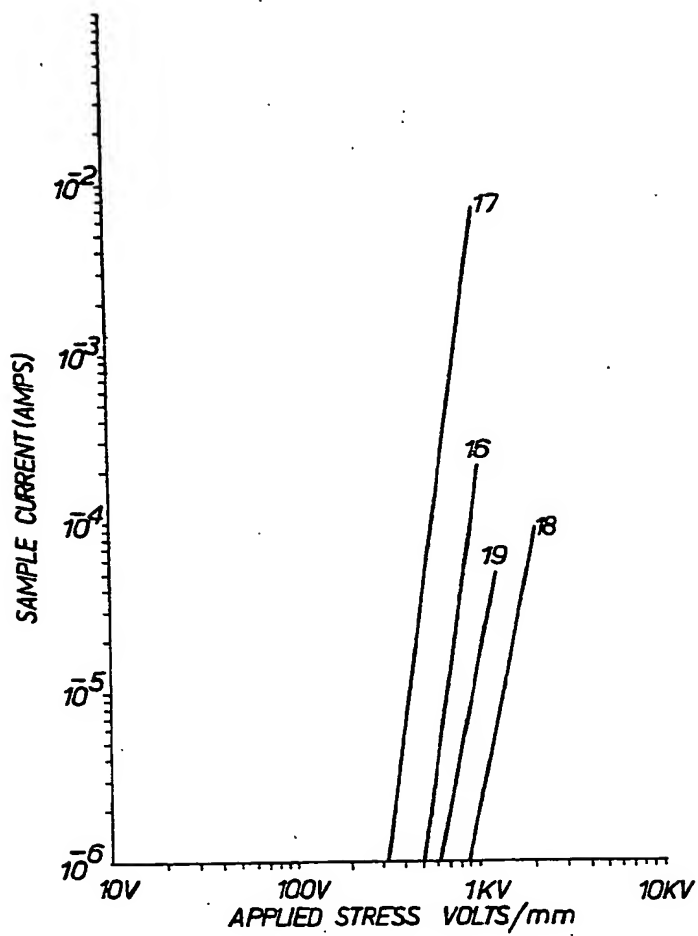


FIG. 8.

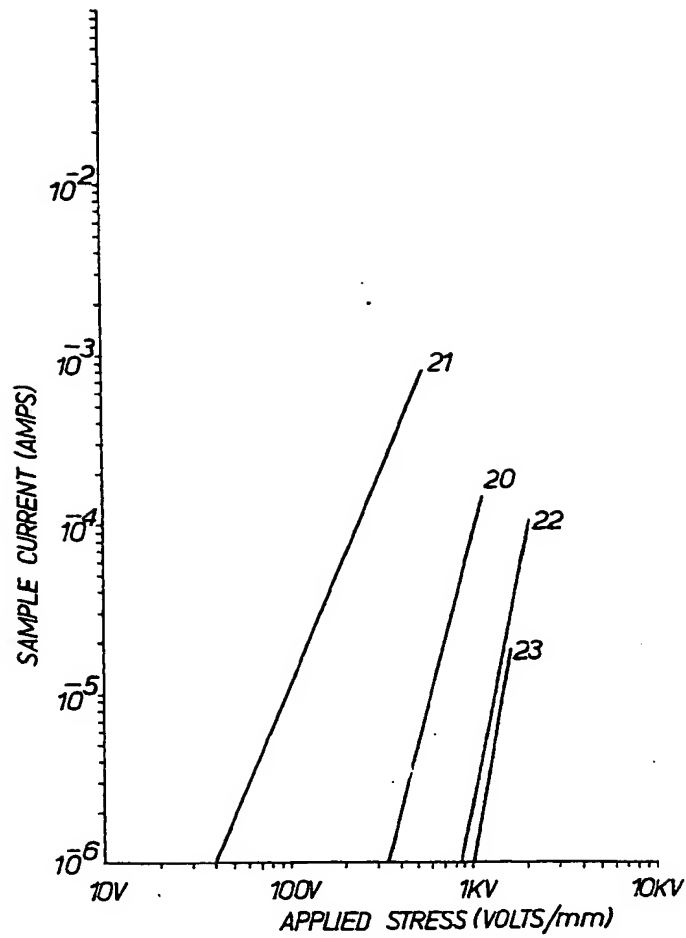


FIG. 9.

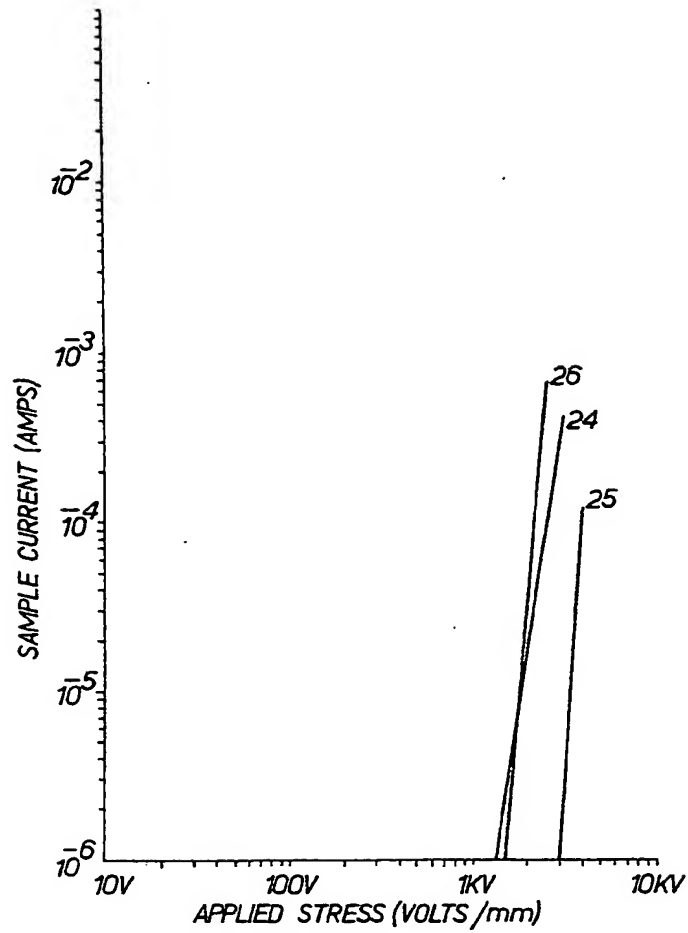


FIG. 10.

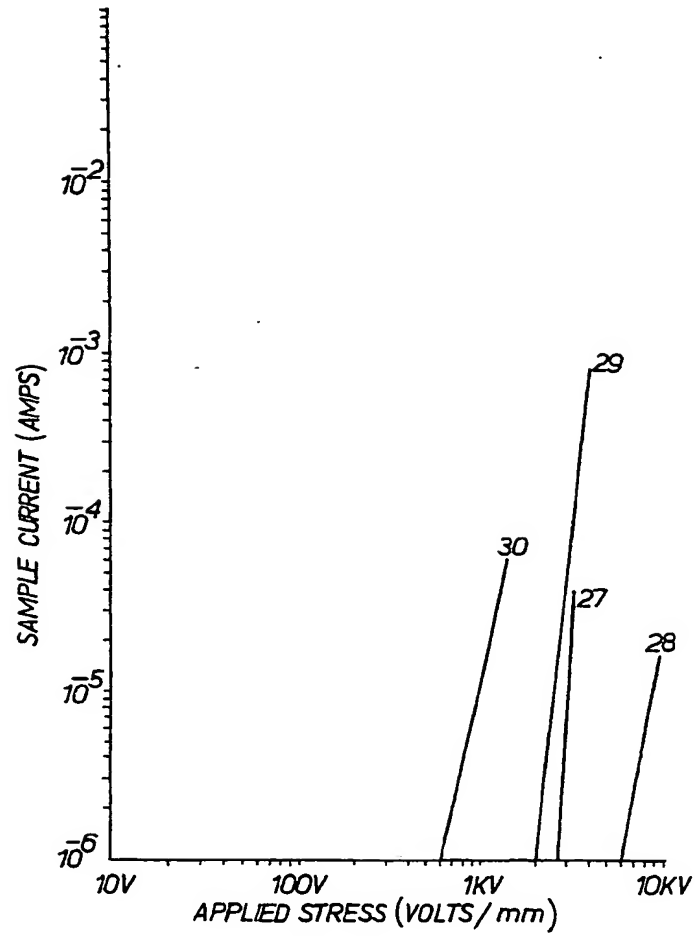


FIG. 11.

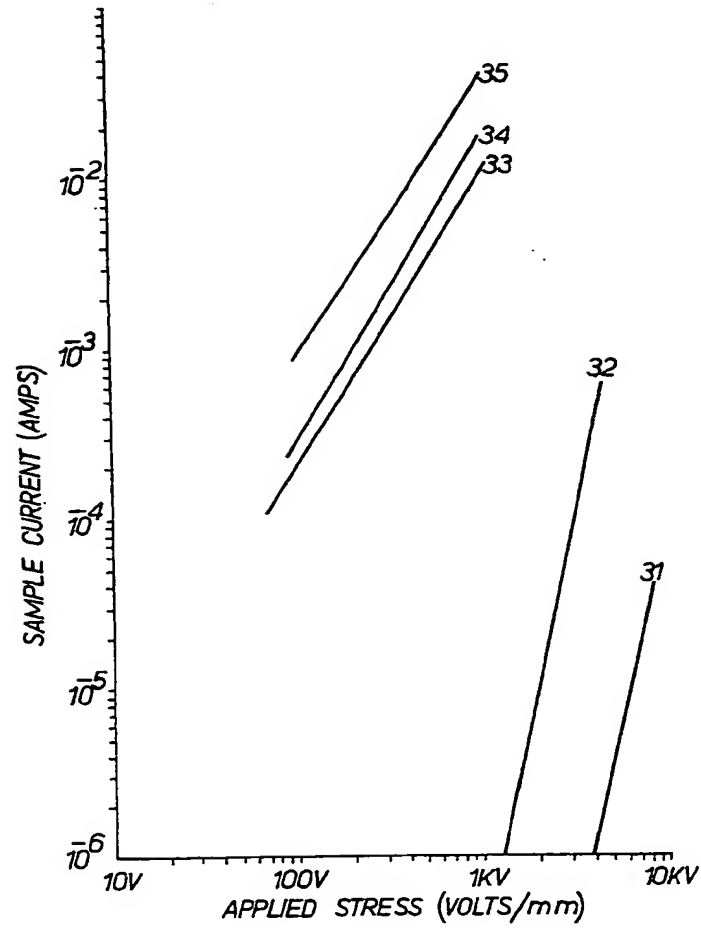


FIG.12.

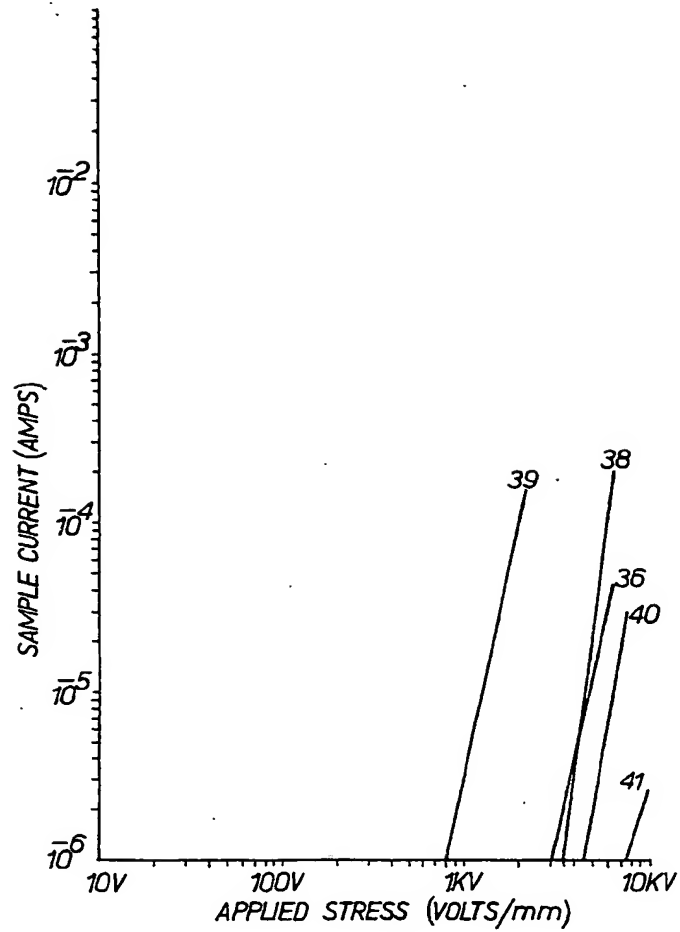


FIG.13.

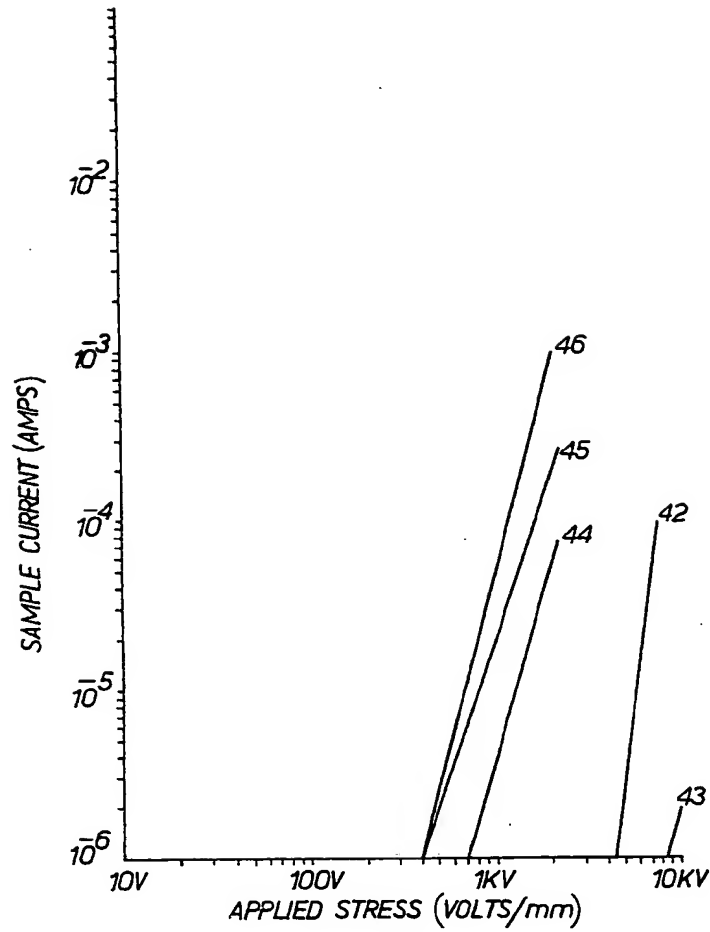


FIG. 14.

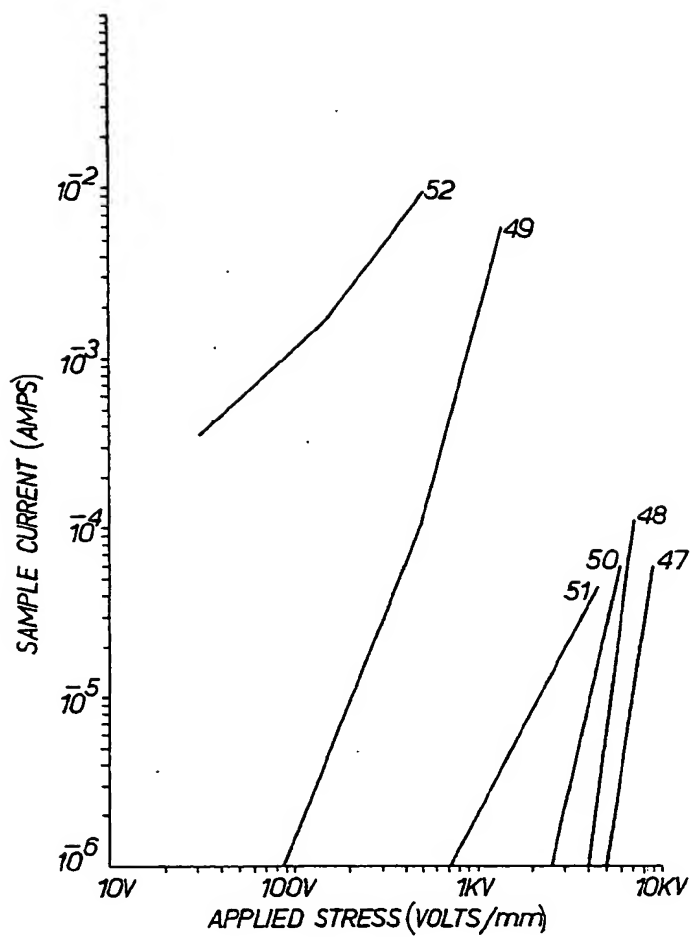


FIG. 15.

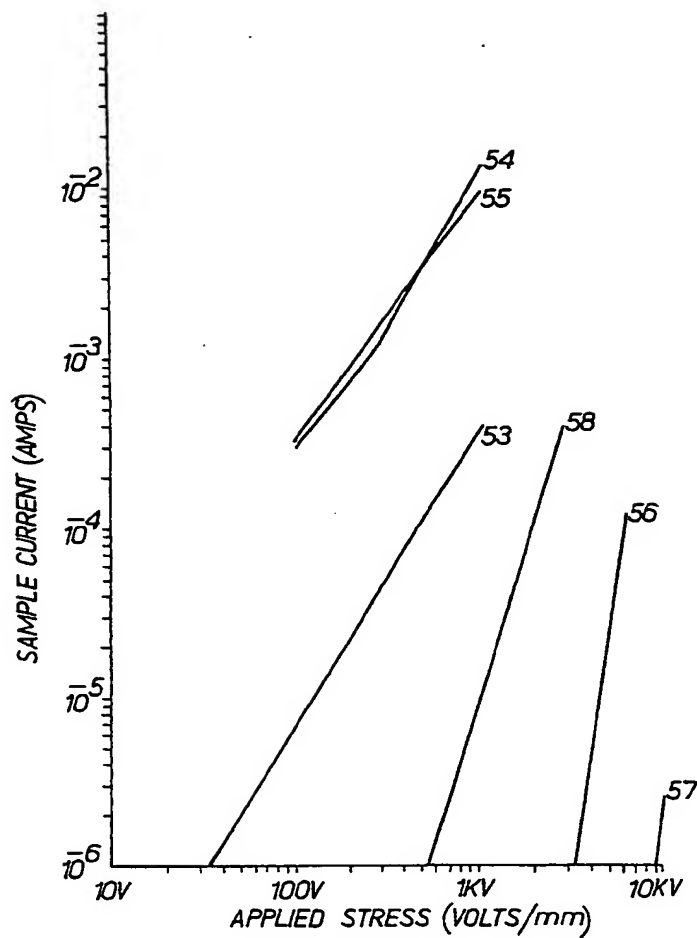


FIG.16.

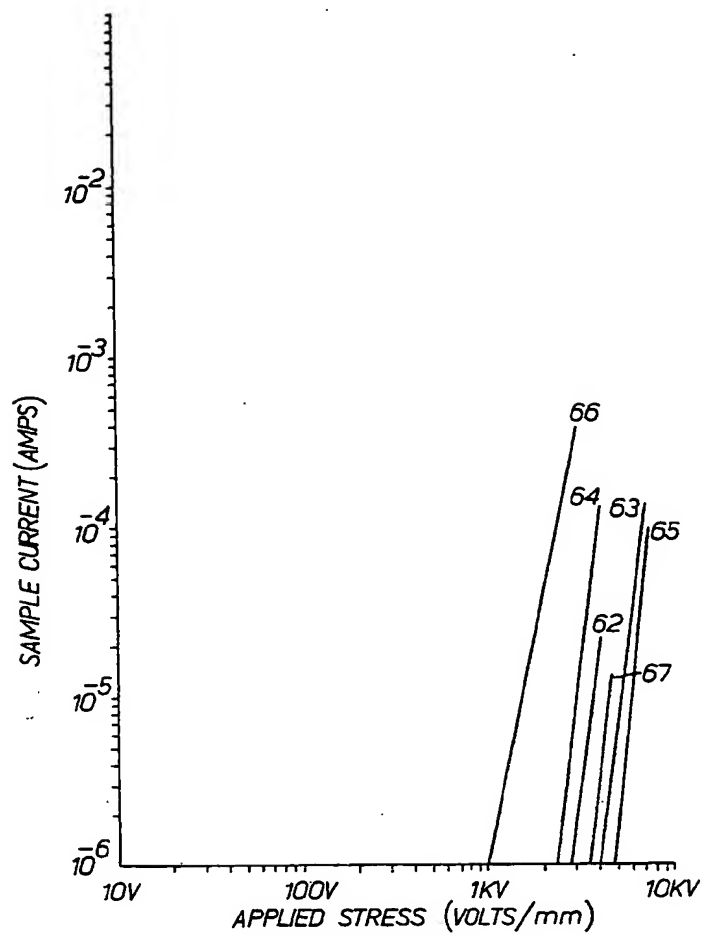


FIG.17

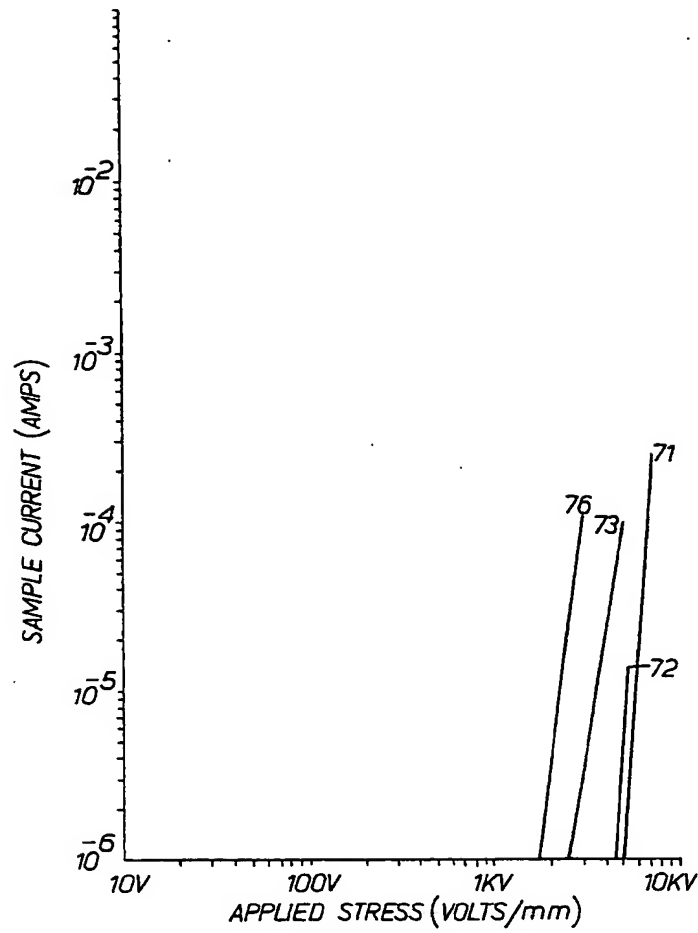


FIG. 18.

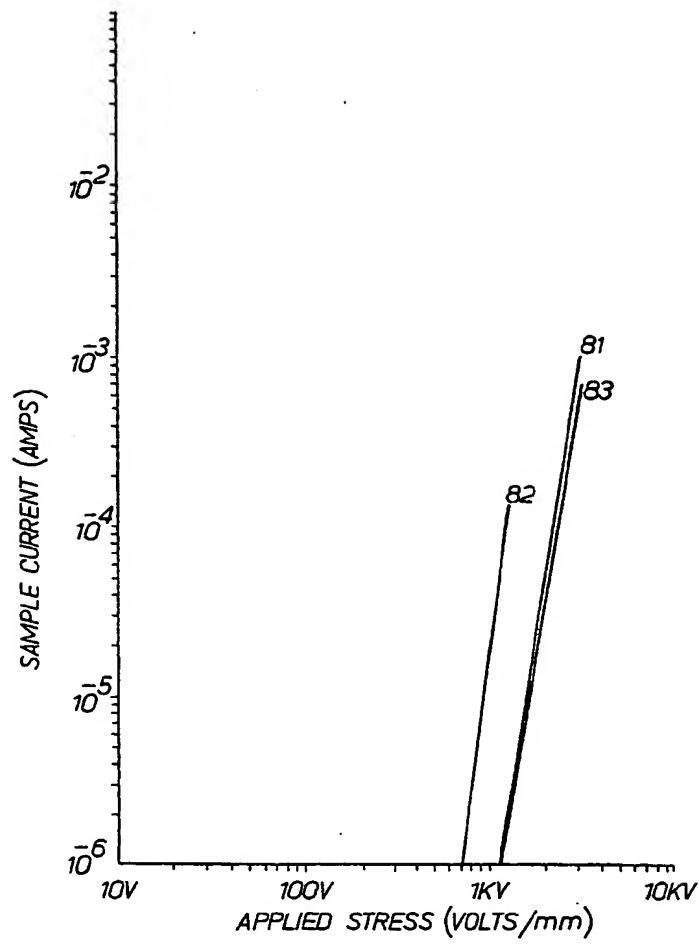


FIG. 19.

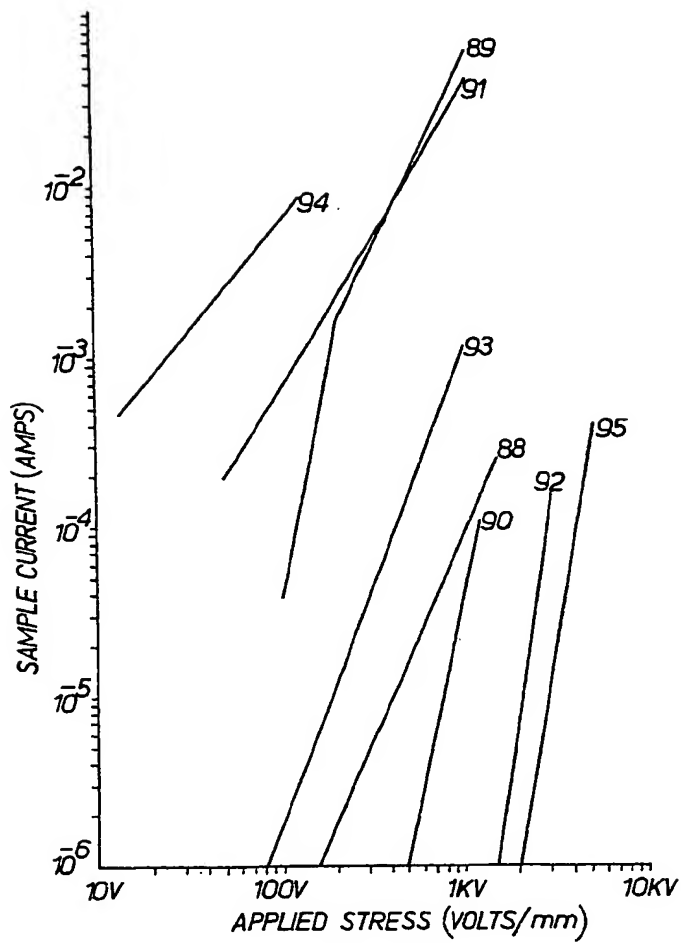


FIG. 20

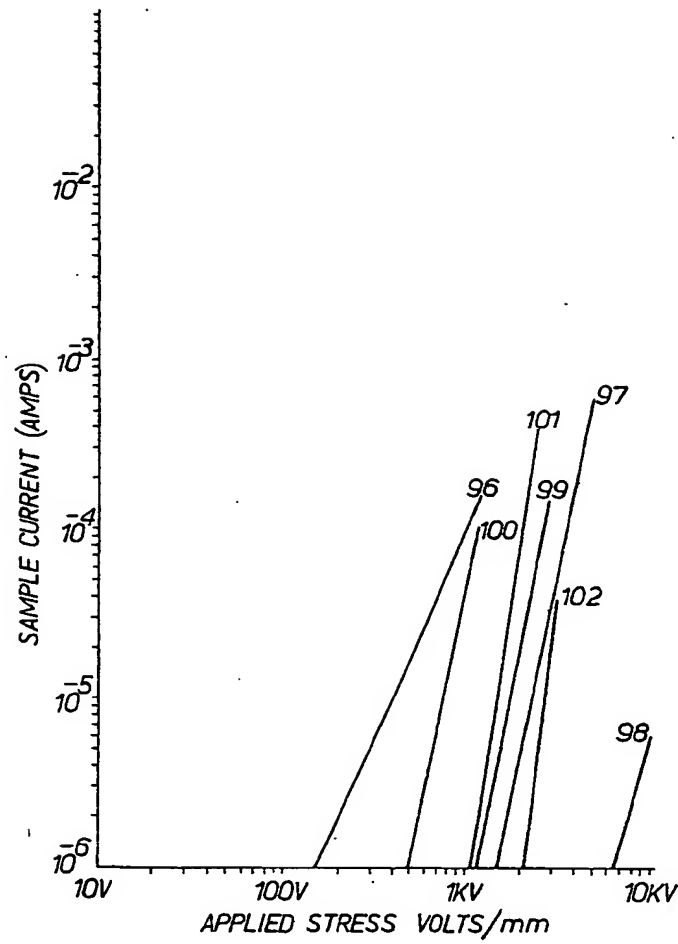


Fig. 21

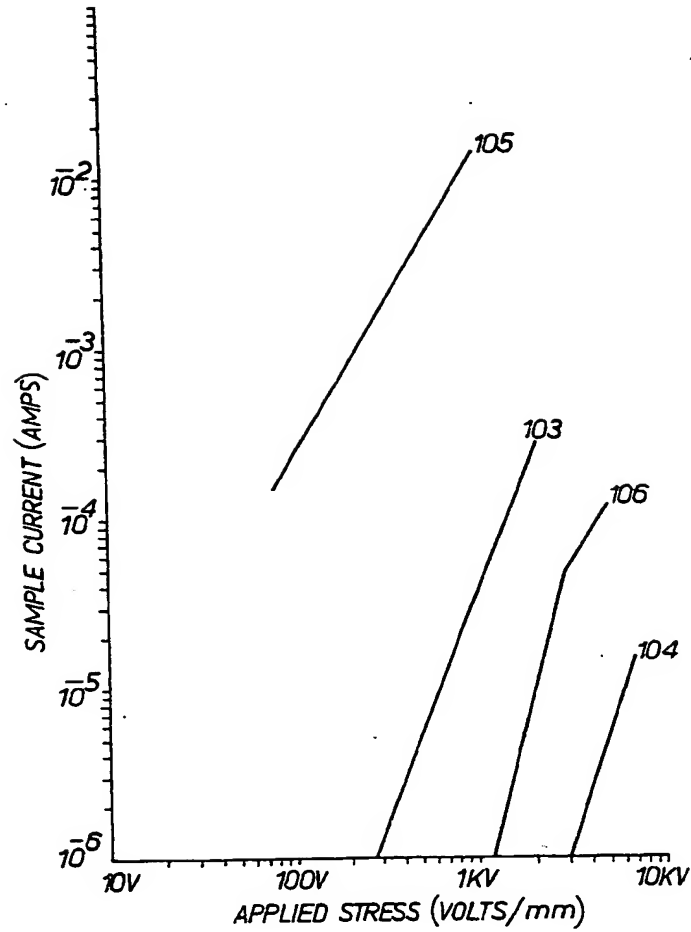
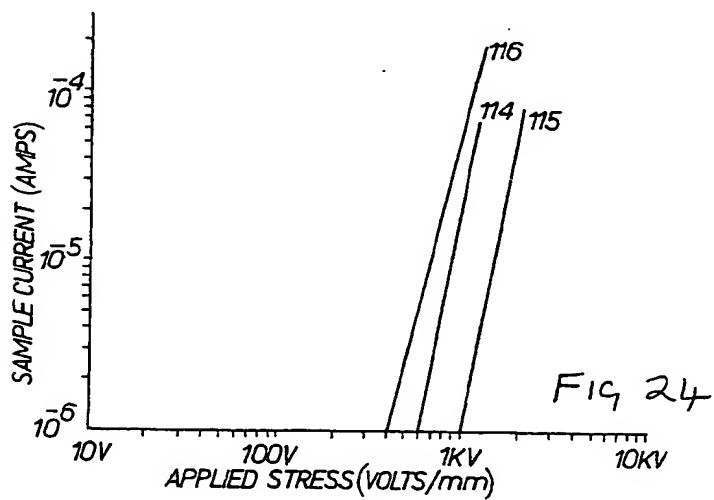
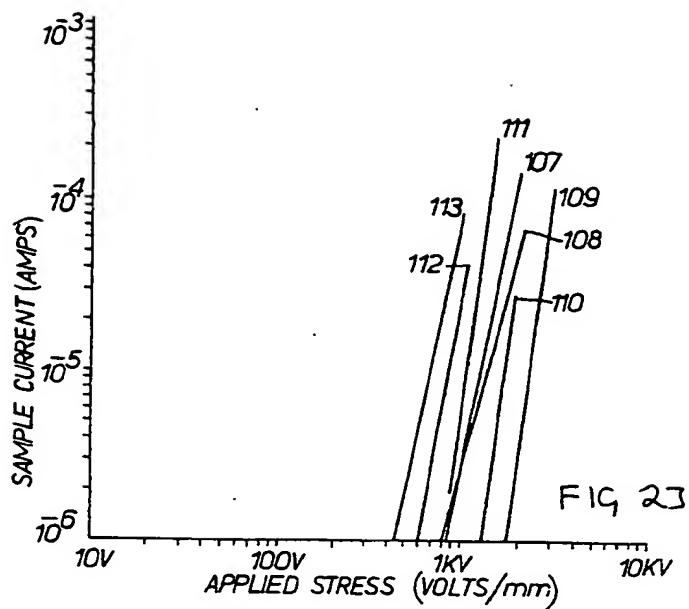


Fig. 22



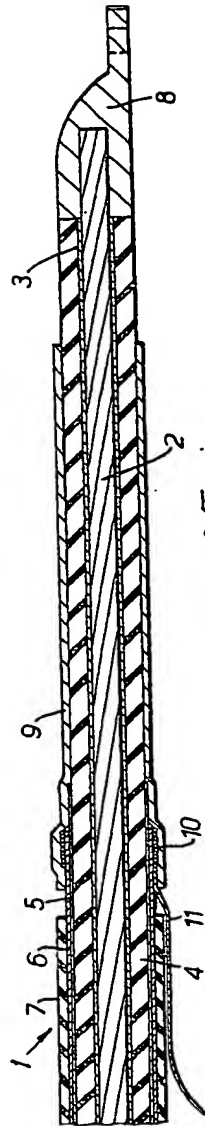


FIG 25

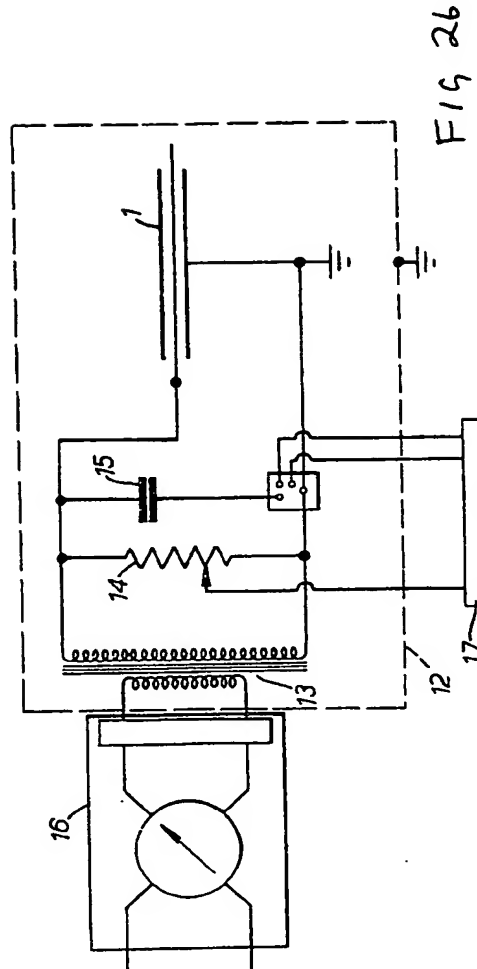
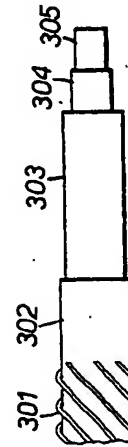
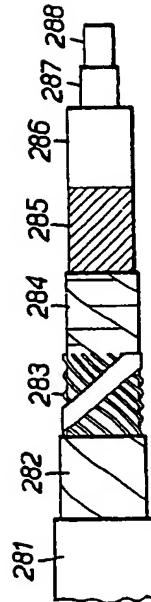
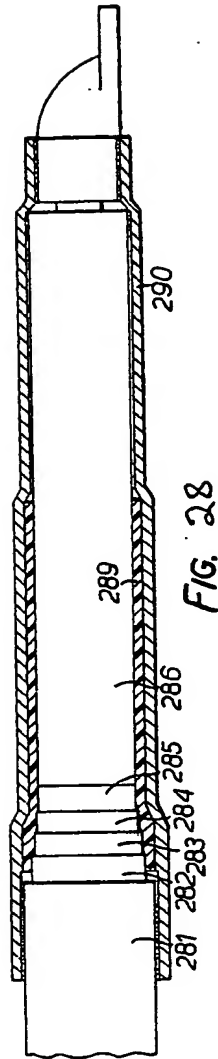


FIG 26



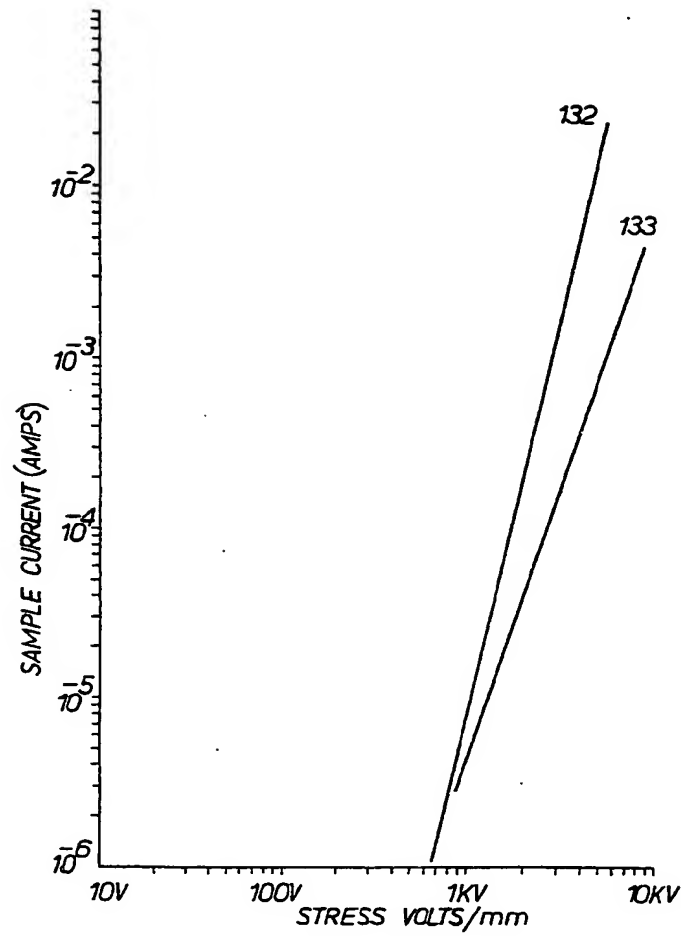


Fig. 30

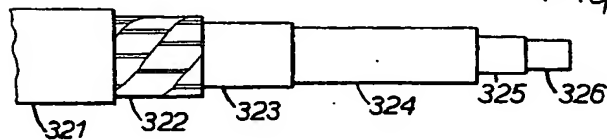


Fig 31

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